

**Supporting information for**

**Enhancement of Polymer Structural Ordering  
in Polymer-stabilized Blue Phases for Improved  
Electro-Optical Properties**

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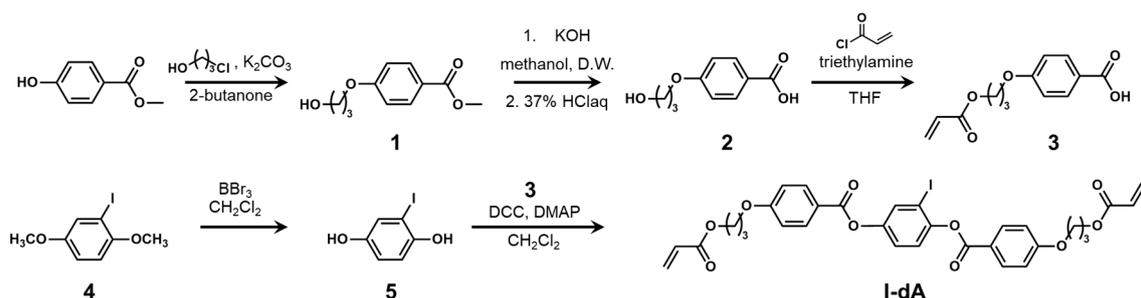
## Materials

All reagents and solvents were purchased from commercial sources and used without further purification. **I-mA**<sup>1</sup>, **I-mMA**<sup>1</sup> and **4**<sup>2</sup> were synthesized as reported procedures.

## Measurements

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on a JEOL JNM-ECX400 apparatus at 400 MHz.

### Scheme S1. Synthesis of I-dA.



### Synthesis of 1

To a solution of K<sub>2</sub>CO<sub>3</sub> (36.3 g, 262.88 mmol) and methyl 4-hydroxybenzoate (10 g, 60.2 mmol) in 2-butanone (155 mL) was added slowly a solution of 1-chloro-3-propanol (6.21 g, 65.72 mmol) in 2-butanone (15 mL). After refluxing 48 h, distilled water (D.W.) was added and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The solution was dried over MgSO<sub>4</sub>, followed by evaporation to afford 12.30 g (83%) of product **1**. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, TMS standard, r.t.)  $\delta$  = 7.90 (d, *J* = 8.9 Hz, 2H), 7.04 (d, *J* = 8.9 Hz, 2H), 4.58 (t, *J* = 5.1 Hz, 1H), 4.11 (t, *J* = 6.3 Hz, 2H), 3.81 (s, 3H), 3.56 (q, *J* = 6.0 Hz, 2H), 1.88 (quin, *J* = 6.3 Hz, 2H).

### Synthesis of 2

A solution of **1** (12.00 g, 53.51 mmol) and KOH (4.50 g, 80.27 mmol) in D.W. (80 mL) and ethanol (113 mL) was refluxed for six hours. After cooling to r.t., to the reaction solution was acidified to pH 2 with 37% HCl aq. and extracted by EtOAc. The solvents were evaporated to afford 8.43 g (80%) of product **2**. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, TMS standard, r.t.)  $\delta$  = 12.64 (s, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 4.61 (s, 1H), 4.11 (t, *J* = 6.4 Hz, 2H), 3.56 (s, 2H), 1.88 (quin, *J* = 6.25 Hz, 2H).

### Synthesis of 3

To a solution of triethylamine (11.2 mL, 80.38 mmol) and **2** (7.80 g, 39.76 mmol) in anhydrous THF (105 mL) was slowly added acryloyl chloride (4.83 mL, 59.63 mmol) under N<sub>2</sub> atmosphere in

the iced bath. The reaction solution was stirred at r.t. for 16 h and at 45 °C for 3 h, and the reaction solution was evaporation to dryness. The residue was solved with CH<sub>2</sub>Cl<sub>2</sub> and the organic layer was washed with 5% HCl aq. and D.W., followed by drying over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Solvents were evaporated and the residue was purified by flash silica gel column chromatography (EtOAc/heptane = 1/1) to afford 6.05 g (65%) of product **3**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS standard, r.t.) δ = 8.05 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 6.42 (dd, *J* = 17.1 Hz, 1H), 6.13 (dd, *J* = 17.1 Hz, 1H), 5.84 (dd, *J* = 10.2 Hz, 1H), 4.38 (t, *J* = 6.3 Hz, 2H), 4.14 (t, *J* = 6.3 Hz, 2H), 2.20 (m, 2H).

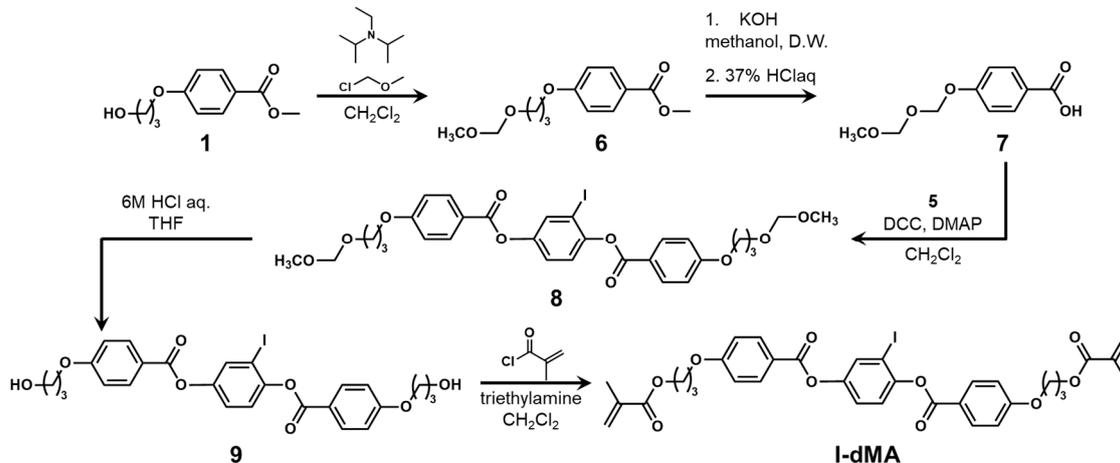
### Synthesis of **5**

A solution of BBr<sub>3</sub> (25 g, 100.35 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (57 mL) was added to a solution of **4** in anhydrous CH<sub>2</sub>Cl<sub>2</sub> at -78 °C. The solution was stirred at r.t. for 12 h and the reaction was worked up by adding iced water. The organic layer was washed with D.W. and dried over anhydrous MgSO<sub>4</sub>. Solvents were evaporated and the residue was purified by silica gel column chromatography to afford 2.28 g (48%) of product **5**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS standard, r.t.) δ = 7.16 (d, *J* = 2.9 Hz, 1H), 6.87 (d, *J* = 8.9 Hz, 1H), 6.76 (dd, *J* = 8.8, 2.9 Hz, 1H).

### Synthesis of I-dA

To a solution of **5** (0.50 g, 2.12 mmol) and **3** (0.50 g, 2.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (70 mL) was added dicyclo hexyl carbodiimide (4.05 g, 19.63 mmol), 4-(dimethyl amino) pyridine (1.70 g, 13.92 mmol). The solution was stirred at r.t. for 24 h, and the solvents were evaporated to dryness after filtration. The residue was purified by silica gel column chromatography, followed by recrystallization from EtOAc/ethanol to afford 0.80 g (57%) of product **6**. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, TMS standard, r.t.) δ = 8.16 (d, *J* = 8.9 Hz, 2H), 8.09 (d, *J* = 8.9 Hz, 2H), 7.89 (d, *J* = 2.3 Hz, 1H), 7.42 (m, 2H), 7.16 (d, *J* = 8.9 Hz, 2H), 7.15 (d, *J* = 8.9 Hz, 2H), 6.36 (dd, *J* = 17.3 Hz, 1.5 Hz, 2H), 6.20 (dd, *J* = 17.3, 10.3 Hz, 2H), 5.96 (dd, *J* = 10.3, 1.5 Hz, 2H), 4.30 (t, *J* = 6.4 Hz, 4H), 4.29 (t, *J* = 6.4 Hz, 4H), 4.21 (m, 4H), 2.14 (q, *J* = 6.3 Hz, 2H), 2.13 (q, *J* = 6.2 Hz, 2H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, TMS standard, r.t.) δ = 166.14, 164.43, 163.89, 163.34, 163.28, 149.00, 148.61, 132.67, 132.40, 132.32, 131.07, 128.45, 123.25, 122.78, 121.38, 121.32, 114.40, 114.36, 90.02, 64.66, 61.13, 28.48., HRMS (EI) Calcd for C<sub>32</sub>H<sub>29</sub>IO<sub>10</sub> [M]<sup>+</sup>: m/z 700.0805. Found: m/z 700.0806.

## Scheme S2. Synthesis of I-dMA.



### Synthesis of 6

To a solution of **1** (16.50 g, 78.5 mmol) and diisopropylethylamine (26.70 mL, 157 mmol) in  $\text{CH}_2\text{Cl}_2$  in iced bath was slowly added chloro methyl ether (7.58 g, 94.2 mmol) and the solution was stirred at r.t. for 12 h. The organic layer was washed with D.W. and extracted by  $\text{CH}_2\text{Cl}_2$ , followed by drying over  $\text{MgSO}_4$ . After evaporating the solvent, the residue was purified by silica gel column chromatography to afford 16.23 g (81%) of product **6**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS standard, r.t.)  $\delta$  = 7.98 (d,  $J$  = 8.7 Hz, 2H), 6.92 (d,  $J$  = 8.7 Hz, 2H), 4.63 (s, 2H), 4.13 (t,  $J$  = 5.8 Hz, 2H), 3.87 (s, 3H), 3.73 (t,  $J$  = 5.8 Hz, 2H), 3.34 (s, 3H), 2.09 (m, 2H).

### Synthesis of 7

A mixture of **6** (16.27 g, 63.98 mmol) and KOH (5.39 g, 95.98 mmol) in D.W. and ethanol was refluxed for 6 h. The reaction mixture was cooled down to r.t. and was acidified to pH 2 with 37% HCl aq. After evaporating the solvents, the residue was purified by recrystallization from methanol to afford 12.95 g (80%) of product **7**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS standard, r.t.)  $\delta$  = 8.05 (d,  $J$  = 8.7 Hz, 2H), 6.95 (d,  $J$  = 9.7 Hz, 2H), 4.64 (s, 2H), 4.16 (t,  $J$  = 6.3 Hz, 2H), 3.73 (t,  $J$  = 5.8 Hz, 2H), 3.35 (s, 3H), 2.10 (m, 2H).

### Synthesis of 8

To a solution of **5** (2.05 g, 86.9 mmol) and **7** (4.13 g, 17.06 mmol) in  $\text{CH}_2\text{Cl}_2$  (25 mL) were added dicyclo hexyl carbodiimide (3.52 g, 170.6 mmol), 4-(dimethyl amino)pyridine (0.42 g, 34.3 mmol), and the mixture was stirred at r.t. for 24 h and filtered. The solvents were evaporated, and the residue was purified by silica gel column chromatography (EtOAc/toluene = 5/95), followed by recrystallization from EtOAc/EtOH to afford 4.35 g (75%) of product **8**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS standard, r.t.)  $\delta$  = 8.22 (d,  $J$  = 8.7 Hz, 2H), 8.13 (d,  $J$  = 8.7 Hz, 2H), 7.73 (s, 1H), 7.28 (s, 2H),

7.00 (t,  $J = 9.2$  Hz, 4H), 4.65 (s, 4H), 4.19 (t,  $J = 5.8$  Hz, 4H), 3.74 (t,  $J = 5.8$  Hz, 4H), 3.36 (s, 6H), 2.12 (m, 4H).

### Synthesis of **9**

A mixture of **8** (4.30 g, 680.48 mmol), 6 M HCl aq. (100 mL) and THF (100 mL) was stirred at r.t. for 48 h. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the solvents were evaporated, followed by recrystallization from EtOAc to afford 2.27 g (61%) of product **9**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS standard, r.t.)  $\delta = 8.22$  (d,  $J = 8.8$  Hz, 2H), 8.13 (d,  $J = 8.8$  Hz, 2H), 7.74 (s, 1H), 7.54 (d,  $J = 8.8$ , 1H), 7.01 (d,d,  $J = 8.8, 9.8$  Hz, 4H), 6.90 (d,  $J = 8.8$ , 1H), 4.23 (t,  $J = 5.8$  Hz, 2H), 4.22 (t,  $J = 6.2$ , 2H), 3.90 (t,  $J = 5.8$  Hz, 4H), 2.10 (quin,  $J = 5.8$ , 4H).

### Synthesis of **I-dMA**

To a solution of triethylamine (1.89 mL, 13.5 mmol) and **9** (2.00 g, 3.38 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (25 mL) under N<sub>2</sub> atmosphere in iced bath was slowly added methacryloyl chloride (0.95 mL, 10.1 mmol) and stirred over night at r.t. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvents were evaporated, and the residue was purified by silica gel column chromatography (EtOAc/CH<sub>2</sub>Cl<sub>2</sub> = 5/95) to afford 1.90 g (77%) of product **I-dMA**. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, TMS standard, r.t.)  $\delta = 8.14$  (d,  $J = 8.7$  Hz, 2H), 8.09 (d,  $J = 8.8$  Hz, 2H), 7.88 (d,  $J = 1.9$ , 1H), 7.43 (m, 2H), 7.17 (d,  $J = 9.0$ , 2H), 7.14 (d,  $J = 9.0$ , 2H), 6.06 (s, 2H), 5.70 (s, 2H), 4.29 (t,  $J = 6.0$  Hz, 4H), 4.22 (t,t,  $J = 5.5$  Hz, 4H), 2.14 (m, 4H), 1.96 (s, 6H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, TMS standard, r.t.)  $\delta = 167.35, 164.44, 163.90, 163.36, 163.30, 149.01, 146.61, 136.21, 132.68, 132.42, 132.33, 125.71, 123.25, 122.79, 121.37, 121.31, 114.39, 114.36, 90.03, 64.76, 61.29, 28.51, 18.35$ . HRMS (EI) Calcd for C<sub>34</sub>H<sub>33</sub>IO<sub>10</sub> [M]<sup>+</sup>: m/z 728.1118. Found: m/z 728.1117.

### References

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